Theoretical and experimental investigation of stereoelectronic interactions in H-complexes of sulfenamide derivatives

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The photoelectron and IR spectra of a number of sulfenamide derivatives and their H-complexes have been investigated. A correlation between an increase in the vertical ionization potential of the lone electron pair of the nitrogen atom and a decrease in the frequency shift of the stretching OH-vibrations in the H-complexes of compounds R_3N, R_2NCH_2OR, R_2NSR, and R_2NSOR was found. The electronic and geometric structures of the starting bases and their H-complexes were calculated by the *ab initio* and MNDO methods. Anomeric interactions were found to decrease the energy of the n(N) orbital and to hinder the formation of H-complexes. The calculations of the sulfenamides and their H-complexes in unstable conformations, characterized by increased energies of H-complexation and proton affinity, were also carried out.

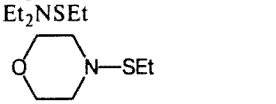
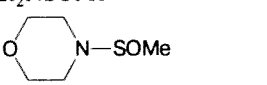
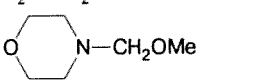
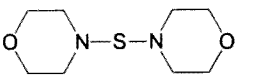
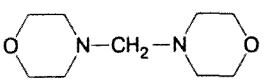
Key words: sulfenamide derivatives; photoelectron spectra; H-complexes, stereoelectronic interactions; *ab initio* and MNDO methods.

Previously,[1–4] we established a relationship between the ionization potentials (IP) of sulfenamide derivatives and the geometric structures of their molecules. In this work, the effect of stereoelectronic n—n- and n—σ-interactions on the electron-releasing properties of sulfenamides, their H-complexing ability and ionization potentials, was studied. The frequency shifts of the stretching OH-vibrations of phenol in H-complexes with sulfenamides were compared to the ionization potentials. For theoretical interpretation of experimental results, calculations of the structure of molecules of the starting compounds, of their H-complexes, and those of the protonated structures by the MNDO method with full optimization of the geometry were carried out. The *ab initio* calculations of the simplest model compounds, H_2NSH and H_2NSOH, were also performed.

A number of works[5–7] have been dedicated to IR spectroscopic analysis of the elecron-releasing properties of bidentate heteroatomic compounds containing an N—X bond (X are the P, S, Se, and Te atoms) and to a search for the center of H-coordination. It follows from those works that the nitrogen atom is the center of the formation of an H-bond. Previously we discussed[8–12] the dynamics of the stereoelectronic effects in the molecules of starting bases, their H-complexes, and their protonated structures (in particular, the transformation of n—n-repulsion into a stabilizing factor in protonation) of hydrazones, hydrazines, phosphine oxides, and thiooxides. It was shown that insignificant variations of the substituents in the hydrazonic fragment $RN—N=CR_2$ change the protonation center, but H-complexation proceeds mainly at the imine N atom.

In Table 1, the frequency shifts of the phenolic OH-vibrations in the H-complexes are compared with

Table 1. The vertical ionization potentials (eV) of the investigated compounds (B) and the shifts of frequencies of the OH-vibrations ($\Delta\nu OH/cm^{-1}$) in their H-complexes with phenol (CCl_4, C_B — 0.1—1 mol L^{-1}, C_{PhOH} — 0.01—0.1 mol L^{-1}, d = 0.1—1 mm; the phenol νOH is 3610 cm^{-1})

Compound	Δν	IP_1	IP_2	IP_3
Et_3N	810	8.03 N	11.34	12.62
Et_2NSEt	260	8.22 N	8.62 S	11.10
	235	8.34 N	8.77 S	9.74
	130			
Et_2NSOMe	240	8.35 S	8.86 N	10.17 O
	235	8.60 S	9.05 N	10.10 O
	120			
Et_2NCH_2OMe	275	8.29 N	9.73 O	11.02
	255	8.64 N	9.74 O	9.90 O
	130			
	230	—	—	—
	145			
	250	8.52 N	9.66 O	11.14
	160			

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the vertical ionization potentials of the starting compounds. It can easily be seen that there is not a relation between the frequency shift of the OH-vibrations with the first ionization potential in all cases, but the correlation with the ionization potential of the lone electron pair orbital of the nitrogen atom (n(N)) is well-defined. The ability to form an H-bond (the frequency shift of the OH-vibration) decreases proportionally to the increase in the ionization potential of the n(N) orbital in the sequence R_3N, R_2NCH_2OR, R_2NSR, and R_2NSOR.

The ionization potential of the n(N) orbital increases and the shift of the absorption band of OH-bonds in the H-complexes decreases if the Et_2N fragment is replaced by a morpholine fragment. A clearly defined spectral picture, indicating that two types of H-bonds (O—H...N and O—H...O) exist in solutions, is observed in the IR spectra of the H-complexes of morpholines. It is not improbable that the nitrogen and oxygen atoms, which are separated in the morpholine ring by three bonds, can act as independent atoms in the course of complexation.

The ionization potentials (see Table 1) were assigned as before[1–4] by analyzing the shapes and the relative intensities of the bands in the photoelectron (PE) spectra of sulfenamide derivatives and comparing them with the ionization potentials of compounds containing either N or S heteroatoms and with a number of model systems. The n(N) orbital characterizes the first ionization potential in aminals[12] and sulfenamides,[1,3] and the second ionization potential in aminosulfenates and aminosulfenylchlorides.[2–4] The inversion of the n(N)- and n(S)-orbitals in aminosulfenates is due to the effective interaction between the n(N) orbital and the vacant orbital of the O—C bond, which stabilizes the n(N) orbital and destabilizes n(S) orbital. According to the *ab initio* calculations in the 6-31G* basis set, the energy of stabilization of the n(N) orbital and that of destabilization of the n(S) orbital for the simplest compounds of this series (H_2NSH and H_2NSOH) is ~0.4 eV. The MNDO method gives analogous results (Table 2).

The second stereoelectronic interaction (which is of paramount importance), the repulsion of the n(N) and n(S) orbitals, also manifests itself in the PE spectra of the sulfenamide derivatives. The n(N) and n(S) orbitals are orthogonal in the stable conformers and have minimum repulsion and, as a consequence, the corresponding bands in the PE spectra overlap, since they have close energies.

Table 2. The energies (e/eV) of the highest occupied MOs and the charges (Q) on the atoms of the model bases (B)

Method	B	$-e_1$(S)	$-e_2$(N)	Q(N)	Q(S)
6-31G*	H_2NSH	10.01	11.31	−0.928	0.129
	H_2NSOH	9.66	11.73	−0.930	0.515
MNDO	H_2NSH	9.90	11.19	−0.351	0.214
	H_2NSOH	9.78	11.44	−0.398	0.382

In the aminosulfenate molecules the repulsion of the lone pair orbitals stabilizes the conformation in which the pairs of the orbitals have orthogonal orientation: n(N) ⊥ n(S) and n(S) ⊥ n(O). The conclusion that this conformation of the molecules plays a dominating role was drawn on the basis of comparison of the ionization potentials of aminosulfenates with those of amines, sulfides, aminals, and other model compounds as well as from the analysis of the shape and relative intensity of the bands.[8–11]

Since the n—n- and n—σ-interactions control the ionization potentials of the sulfenamide derivatives and the value of the ionization potential of the n(N) orbital itself (which changes in proportion to the frequency shifts of the OH-vibrations), one can assume that stereoelectronic interactions would also affect the energy of H-complexation. It is known that there are some restrictions in applying the MNDO method to investigations of H-bonds.[13] The bond lengths are overestimated while the energies of the H-bonds are underestimated. However, it can be used to describe the relative ability of related compounds to form H-bonds at heteroatoms of the same type. This is illustrated by Table 3, in which the energies of formation of H-complexes of model compounds (calculated by MNDO and *ab initio* methods) are compared. All the versions indicate weakening of H-complexation under the effect of an SH group, though the absolute values of the energy differ substantially.

Actually, the total energy of the H-complex calculated by the MNDO method exhibits a number of minima differing in their depth in accord with the position of the proton donor molecule HF. Of those minima, there is a local minimum in the vicinity of the nitrogen atom, characterizing the energy of the H-complexation at this atom. According to calculations, the energy of the H-coordination (E_H) at the nitrogen atom decreases as the energy of the n(N) orbital increases. The results of such a calculation for Me_2NR are given below.

R	Me	CH_2OMe	SMe	SOMe
E_H/kcal mol^{-1}	0.90	0.74	0.37	0.36
$-e$[n(N)]/kcal mol^{-1}	9.59	9.76	9.85	10.07

This manifests itself in experiments as an increase in the ionization potential of the n(N) orbital and a decrease in the frequency shift of the OH-vibrations in the H-complexes with the following compounds: R_3N, R_2NCH_2OR, R_2NSR, and R_2NSOR.

Table 3. The energies of formation of the H-complexes BHF (B is base) (E_H/kcal mol^{-1})

B	*Ab initio*			MNDO
	3G	6-31*	MP2/6-31*	
NH_3	10.2	12.6	14.1	1.5
H_2NSH	4.0	9.3	12.3	1.2

Table 4. Energies of H-complexation, proton affinity (kcal mol^{-1}), charge on the nitrogen atom (Q), and energies (e/eV) of the highest occupied MOs calculated by the MNDO method

B	Version*	E_H	The proton affinity	Q	$-e_1$	$-e_2$
Me_3N	*A*	0.9	156.7	−0.438	9.59 N	13.16
Me_2NCH_2OMe	*A*	0.7	156.3	−0.438	9.76 N	11.04 O
	B	0.6	158.3	−0.473	9.50 N	11.38 O
Me_2NSMe	*A*	0.4	150.5	−0.491	9.54 S	9.85 N
	B	1.2	153.6	−0.469	8.79 SN	11.00 NS
Me_2NSOMe	*A*	0.4	148.4	−0.574	9.54 S	10.07 N
	B	1.3	156.3	−0.540	8.77 SN	10.85 NS

* *A* — full optimization of the geometry, *B* — ϕ(XNSO) = 90°.

In the case of Et_2NR the following experimental data were obtained.

R	Et	CH_2OMe	SEt	SOMe
$\Delta\nu$OH/cm^{-1}	810	290	270	240
IP [n(N)]/eV	8.03	8.29	8.22	8.86

The values of E_H were calculated from the relationship:

$$E_H = E(B) + E(HF) - E(BHF),$$

while the values of E(BHF) were found from optimization of all the geometric parameters (B is the base).

Thus, the MNDO method reproduces the experimental succession of the ionization and H-complexation energies. In our opinion, this indicates that the MNDO method can be applied to theoretically analyze the role of the stereoelectronic interactions in the formation of H-complexes of the compounds under study. For this purpose we performed a computer simulation: the starting bases, the H-complexes, and the protonated structures were calculated in stable conformations with full optimization of geometric parameters (version *A*) and in unstable conformations in which the n(N) and n(S) orbitals are parallel while the n(N) and σ(S—R) orbitals are orthogonal (version *B*, Table 4). The differences between the total energies of the bases (B), of their H-complexes, and of the protonated structures, calculated for versions *A* and *B*, were used to estimate the total contribution of the n—n- and n—σ*-interactions to stabilization (destabilization) of the corresponding conformers and to compare the deactivating effect of functional groups and of the methyl group on H-complexation.

As mentioned above, the repulsion of the n(N) and n(S) orbitals is minimum, and the two-electron n—σ*-stabilization is maximum in the stable conformers (version *A*, see Table 4). At ϕ = 90° (version *B*), the repulsion of the lone pair orbitals is maximum, and the n—σ-interaction is minimal. The destabilizing factor (the repulsion between the n(N) and n(S) orbitals) disappears after protonation, since the σ(N—H) bond is formed and additional stabilization of the cation due to interaction of the n(S) orbital with the σ*(N—H) orbital arises due to the n(N) orbital.[8] The transformation of the destabilizing stereoelectronic interaction into stabilizing interaction after H-complexation is not so pronounced as that which occurs after protonation (Table 5).

Table 5. Difference ($\Delta E = E(B) - E(A)$, kcal mol^{-1}) between the total energies of bases (B), H-complexes, and protonated structures for versions *A* and *B*

Compound	B	BHF	BH^+
Me_2NCH_2OMe	3.6	3.7	1.9
Me_2NSMe	8.9	8.1	3.2
Me_2NSOMe	10.3	9.4	2.2

We note that according to calculations,[2,14] the stereoelectronic interactions are strongest in the starting bases, they are somewhat weaker in the H-complexes, and they are weaker still in the protonated structures. In our opinion, a decrease in the stereoelectronic stabilization of the H-complexes is the main reason for the decreased complexing ability of sulfenamides and other bidentate compounds containing two adjacent heteroatoms (N—S, P—N, P—S).

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